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(54) **Use of inorganic particles and method for marking and identifying a substrate or an article**

Verwendung von anorganischen Teilchen und Verfahren zur Markierung und Identifizierung eines Substrats oder Artikels

Utilisation de particules inorganiques et procédé de marquage et identification d'un substrat ou article

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**EP 0 927 750 B1**

## Description

- [0001] This invention relates to the use of inorganic particles which comprise at least two chemical elements in a predefined and analytically identifiable ratio, a method for tagging a substrate and to a method of tagging and identifying a substrate and/or an article.
- [0002] Encoded micro-particles whose code is represented by at least three visually distinguishable coloured layers of organic resins and their use as tag and/or security feature in order to prevent counterfeiting of articles have already been described in DE 26 51 528 and US 4,329,393. Originally, these particles have been developed to allow tracing of explosives from production to detonation. These tags are sold under the trade name Microtaggant or Microtrace.
- [0003] As the colour sequence of the layers is the only coding feature, particle size and material selection limits the application of these tags. Particle size below 30pm is a necessary requirement for many applications, particularly printing inks and related products. Highly resolved lines and figures are difficult to produce with printing inks containing particles larger than the printed feature itself. Particles made of organic laminate can hardly be ground down to sizes in the desired range.
- [0004] A further disadvantage of these organic particles is their lack of heat resistance. This results in the destruction of a tagging or security element when the article is exposed to fire or heat.
- [0005] US 5,670,239 discloses a composition for the delocalized marking of articles, which makes the forging or improper exploitation of these articles difficult. The composition contains non-ubiquitous chemical elements, i.e. more or less rare elements from the main- and sub-groups of the periodic system. In particular these are elements which have an X-ray  $K_{\alpha}$  line in the range between 3.69 keV and 76.315 keV and which may be present either in elemental form or in the form of any desired compound.
- [0006] The elemental compositions and their concentrations serve as delocalized stored information which cannot be discerned with the naked eye. An information item, e.g. an encrypted numerical code or a number/letter combination, can be represented by a set of specific elements or compounds, where each specific element or compound represents a digit of the code, and the concentration of the element or compound expresses the value of that digit, e.g. the figure or the letter. If a specific element or compound belonging to the set is absent from the composition, then the value of the corresponding digit is zero or blank.
- [0007] US 5,670,239 shows several shortcomings. This marking method requires in any case the retrieval of precise concentrations for the marking composition components in the marked bulk materials, coatings or printing inks. This depends on a homogenous distribution of the marking components which are provided generally as solution. Finding compounds of all desired elements which dissolve homogeneously in a coating composition over the whole required concentration range without forming precipitates is rather difficult.
- [0008] Also the use of mixtures of solid state materials is precluded due to their inherent tendency to segregate according to particle size, specific gravity, etc..
- [0009] An additional disadvantage is the restricted range of coding possibilities, since each specific chemical element or compound can only represent a n-valued digit of the code. The total coding capacity for m specific elements is therefore given by  $n^m$ . The restricted coding capacity is due to the fact that in a delocalized coding system only chemical information is evaluated. The code may thus be broken by any sufficiently sensitive analytical method which is able to yield quantitative results, i.e. classical elementary analysis, X-ray fluorescence, Laser-Ablations-ICP-MS etc.. That makes the decoding and reverse-engineering for any potential counterfeiter easy.
- [0010] A further disadvantage of the teaching of US 5,670,239 is the sensitivity of the encryption to perturbing elements. One or more of the elements used for the encryption may accidentally be present for another reason in or on the marked object. This will impede a proper readout of the encoded digit. Perturbation of other security systems can, *vice versa*, occur by the presence of this type of encoding, in particular if soluble compounds of rare-earth ions are employed, which are often luminescent in the visible or infrared domain of the spectrum. This kind of interferences are likely to occur with security documents, where a plurality of security systems has to be combined.
- [0011] It is therefore an object of the present invention to provide marking means which do not show the drawbacks of the prior art and which are particularly suitable for application on security documents.
- [0012] It is a further object of the invention to provide a reliable forensic tool for marking articles against counterfeiting or improper use.
- [0013] Another object of the invention is to provide marking means which are compatible with the existing security systems, especially those which are in use on security documents and which serve for their automated machine recognition.
- [0014] Another object of the invention is an increase of the coding capacity.
- [0015] Another object of the invention is to provide an encryption which makes the reverse-engineering difficult and which can not be broken by most of the commonly available analytic tools.
- [0016] Another object of the invention is to provide marking means which are insensitive to perturbing elements.
- [0017] Another object of the present invention is to provide marking means which do not depend on the formation

of homogeneous mixtures with the base material or materials of the article, or with the coating or printing ink to be marked.

[0018] These objects were solved by the features of the independent claims.

[0019] Particularly they were solved by the use of at least one type of inorganic particle comprising at least two chemical elements in a predefined and analytically identifiable ratio as a marking means.

[0020] These particles are introduced into or applied onto the article as a marking mean. The specific ratio of elements in that inorganic particle, which is characteristic for each type of particles, represents a code, or part of a code.

[0021] The information containing particles can be localized by scanning electron microscopy (SEM) using back-scattered electron detection.

[0022] Thus, the sites, i.e. the particles where information is contained, must be localized in a first step. Subsequent to the localizing of the information containing particle, the ratio of chemical elements being comprised in that particle can be determined by energy- or wavelength-dispersive X-ray analysis (EDX). Both steps, i.e. the localizing of a particle and its analysis are performed on the same SEM equipment. The proper decoding of the marking according to the present invention is tied to analytical methods combining both, microscopy for the localizing, and elemental analysis for the reading of the code. By concentrating the coded information to at least one localized particle, the information retrieval is not dependent on homogeneous mixing. For the reading of such markings SEM/EDX is the best practicable method today. For SEM/EDX, a particle volume in the order of  $0.01 \mu\text{m}^3$  is sufficient to be properly read.

[0023] A further beneficial property of the SEM/EDX analysis method is its dependency upon standards in order to get reliable quantitative results. The quantity of an element present in a particle is determined from the intensity of its characteristic X-ray emission. This latter, however, depends upon the precise excitation conditions i.e. the energy of the exciting electron beam. As the energy of the exciting beam is more or less attenuated in function of the density of the material, the analysis must be performed against standard materials of similar chemical nature. In the absence of such standards, the quantitative results can be quite wrong. In security applications, the standards and their exact compositions are known to the owner of the marking, but not to the counterfeiter. The counterfeiter must therefore rely on indirect evidence, and will therefore not be able to copy the marking, even if he had at his disposition an SEM/EDX equipment and a performing materials synthesis facility.

[0024] The marking particles can contain any chemical element.

[0025] Particularly useful are elements of the second half of the periodic table as they facilitate the localization of the particle on the SEM. However, for coding purposes, one can use any element with an atomic number of at least five. Those elements are readable by the above mentioned detection and analysing devices.

[0026] The encoding compounds used in the present invention are preferably chosen among the non-stoichiometric crystalline compounds or among the different types of glasses. Not with quite the same security potential, however satisfying for selected applications, are stoichiometric crystalline compounds. Stoichiometric compounds are such which do only exist in a defined elemental ratio. Calcium carbonate ( $\text{CaCO}_3$ ), Quartz ( $\text{SiO}_2$ ), Baryte ( $\text{BaSO}_4$ ), etc. are examples of stoichiometric compounds.

[0027] Non-stoichiometric crystals are solids with a microscopically ordered structure, i.e. the atoms are arranged in a regular fashion, called the crystal structure. Certain crystal structures are quite tolerant towards replacement of one type of atom by another without the need for changes in their microscopic order, given that certain general rules like atom sizes and charge neutrality are respected. Examples of such structure types are the spinels ( $\text{AB}_2\text{O}_4$ ) the garnets ( $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$  or  $\text{A}_3\text{B}_5\text{O}_{12}$ ), the perovskites ( $\text{ABO}_3$ ), the lanthanide oxysulphides ( $(\text{Y}, \text{Ln})_2\text{O}_2\text{S}$ , the zircones ( $\text{ABO}_4$ ) etc. Here A, B, C stand for the different types of sites encountered in the crystal structure; these sites must be occupied by corresponding metal ions. Ln stands for the lanthanide series, i.e. elements 57 to 71. A given site in all these structures may be occupied either by a single type of metal ion, or by a mixture of different types of chemically similar metal ions. For example, the compounds  $\text{Fe}_3\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $(\text{Zn}_x\text{Co}_{1-x})\text{Fe}_2\text{O}_4$  and  $\text{Co}(\text{Fe}_{2-x}\text{Al}_x)\text{O}_4$  all possess the spinel structure. The parameter x in certain of these formulas may be freely chosen, i.e. one or more concentration ratios exist which are not prescribed by stoichiometry. The present invention relies heavily on the existence of this type of compounds for the realization of suitable information containing particles.

[0028] Glasses are non-crystalline solid state materials, characterized by the absence of microscopic order. At the atomic level, the structure of a glass resembles that of a liquid. One could therefore describe a glass as being an extremely viscous liquid at room temperature. The composition of a glass can be changed to a large extent; and a great variety of additional metal ions can be introduced (dissolved) into the glass forming base material. Such glass formers are known in the field of oxides ( $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$ , etc.), of fluorides ( $\text{BeF}_2$ , etc.), of nitrides, etc.. Glass compositions are non-stoichiometric per definition, as they do not have a crystal structure with respect to which stoichiometry could be defined. The only limiting factor in glass formation is solubility, i.e. if all desired constituents are able to mix up homogeneously in a single melt and to stay so during cooling down. Very exotic glasses are feasible for marking purposes in the present invention, e.g. glasses containing Si, Ge, Al, La, Ta, Er and O in various elemental ratios. Glasses can be ground to the desired particle size, although such grinding requires enhanced technology, if very fine particles in the order of 3 - 5  $\mu\text{m}$  are to be achieved.

[0029] In another embodiment the particle is of metal alloy such as alnico, brass, bronze, etc..

[0030] All types of particles can either be used exclusively or in any desired combination.

[0031] One embodiment of the present invention is that the information containing particle consists of superposed layers which comprise the chemical elements in non-stoichiometric or stoichiometric form.

5 [0032] The inorganic particles can be of any shape, including irregularly formed as well as regularly formed particles. The size of said particles is substantially in a range of between 0.1 to 30 micrometers, preferably in a range of between 0.5 to 10 micrometers and even more preferably in a range of between 1 to 5 micrometers. Substantially means that 80 % or more of the total weight of the material falls within the range. The volume of the individual particles is substantially comprised within the range between  $0.01 \mu\text{m}^3$  to  $10000 \mu\text{m}^3$ , preferably within the range of between  $0.1 \mu\text{m}^3$  to  $1000 \mu\text{m}^3$ , more preferably within the range of between  $1 \mu\text{m}^3$  to  $100 \mu\text{m}^3$ .

10 [0033] The inorganic particles of the present invention can be blended into any carrier medium which is able to form stable dispersions of said particles and to hold the particles in place for localization and analysis. Preferably those particles are blended into any kind of coating composition and printing ink which are applied onto any kind of substrate to be marked. In a preferred embodiment, if the coding has to remain invisible to the human eye, the film forming carrier medium is chosen to be transparent in the visible range of the electromagnetic spectrum. In a further application mode, the particles are incorporated into bulk materials which thereafter will obtain their desired form by extrusion, casting, injection moulding, rolling, etc.. Coating compositions or printing inks comprising said particles can be applied to the underlying substrate by any of the known techniques. These include spraying, brushing, dipping, printing. Printing can be performed e.g. by intaglio, gravure, offset, silkscreen, letterpress, flexography and related techniques.

20 [0034] The information containing particles can also be incorporated into powder coating compositions, toners, etc., as well as into paper, security foils, plastic sheets and into fibre, in particular for valued papers, banknotes, checks, etc., and for security documents, passports, driving licences etc.. They can furthermore be used in credit cards, ID-cards, access cards and all other type of cards conferring a right or carrying a value.

25 [0035] The useful amount of particles necessary for a reliable detection and analysis ranges from 0.0001 % to 10 %, preferably from 0.001% to 1% and even more preferably from 0.01% to 0.1% by weight of the total weight of the overall composition or material to which it is added.

30 [0036] The protection against counterfeiting is enhanced when said particles additionally have luminescence-, magnetism-, IR-absorption-, radio frequency- and/or microwave resonance-properties. Coating compositions and/or printing inks can be applied to any security document to prevent counterfeiting or unauthorised trade and use of said document.

[0037] The reading of the codes according to the present invention can be done with any currently available scanning electron microscope (SEM), foreseen that it is equipped with a backscattered electron detector and an energy- or wavelength-dispersive X-ray detector. The data of the examples below stem from three different instruments (a LEO 435VP, a Philips XL30W and a Hitachi S-3500N), which could be used indiscriminately for the same purpose.

35 [0038] In scanning electron microscopy, the sample is scanned by a very fine focused electron beam, of 5 to 10 nm spot size and 1 to 30 kV electron energy. When this primary beam hits the sample, different types of secondary radiation are produced which can be detected with the help of appropriate devices. A plot of the corresponding detector intensity as a function of the scanning electron beam's co-ordinates yields the SEM picture. Depending upon the electron energy and the sample density, the primary beam penetrates more or less into the sample material. For example, a beam of 40 20 keV penetrates about 5 to 8  $\mu\text{m}$  into an organic ink matrix.

[0039] The most important types of secondary radiation are:

45 (i) Secondary electrons, i.e. electrons of the sample material which are ejected after collision with electrons of the primary beam. Secondary electrons have low energies (lower than 50 eV), and can therefore only escape from the very surface of the sample. As a consequence, secondary electron detection yields a surface topographic image of the sample ("topographic contrast").

50 (ii) Backscattered electrons, i.e. electrons of the primary beam which are scattered at the nuclei or cores of the sample atoms. Backscattered electrons have high energies, close to the energy of the primary beam, and can escape from the whole penetrated sample volume. As the electron scattering power of an atom increases with its atomic number, backscattered electrons yield an image of the chemical nature of the sample ("chemical contrast").

55 (iii) X-rays, resulting from the refilling of the sample atoms' vacant electron shells after collisions with electrons of the primary beam. Each atom emits its characteristic X-ray spectrum, consisting of K, L, M, etc. line series, which can be used to conclude to the presence of a certain chemical element in the sample, as well as to determine its relative amount, if a comparison standard is available. The intensity of the received X-ray emission depends notably upon the energy of the exciting primary electron beam, as well as upon the presence of X-ray absorbing material in the ray path. As a general rule, the scanning electron beam energy has to be about at least the double

of the energy of the emission lines to be observed, and emission lines with energies lower than 2 keV will already suffer absorption losses in an organic ink matrix. A usual primary beam energy in SEM work is 20 keV. Under these conditions, elements up to about bromine (atomic number 35) can be determined preferably on their K-lines, whereas the elements from rubidium to bismuth (atomic numbers 37 to 83) have to be determined preferably on their L-lines. For the heavier elements of the latter group, the M-lines are also of some interest, and they serve preferably for the determination of the actinides. For the calculation, the peak areas of the K-, L- and M-line series are separately integrated and taken into account according to the device-specific calculation methods.

**[0040]** The following figures and examples will further explain the present invention which, however, is not limited to them.

Figure 1 shows a SEM picture of a crystalline non-stoichiometric inorganic information containing particle of the present invention, incorporated in a printed intaglio ink, under backscattered electron detection ("chemical contrast").

Figure 2 shows a SEM picture of several crystalline non-stoichiometric inorganic information containing particles of the present invention in a printed optically variable silk screen ink.

Figure 3 shows a SEM picture of the same particles as in Figure 2 in a printed optically variable intaglio ink.

Figure 4 shows a SEM picture of a bulk quantity of crystalline non-stoichiometric inorganic information containing particles, visualized by backscattered electron detection.

Figure 5 shows the energy dispersive X-ray spectrum of one of the crystalline non-stoichiometric particles localized in Figure 2.

Figure 6 shows a table of SEM/EDX analyses, obtained on inorganic particles according to the invention.

Figure 7 shows a SEM picture of inorganic information containing particles of the glass type, according to the present invention.

Figure 8 shows the energy dispersive X-ray spectrum of one of the particles of Figure 7. The chemical composition is  $(\text{GeO}_2\text{-SiO}_2\text{-La}_2\text{O}_3\text{-Er}_2\text{O}_3\text{-Ta}_2\text{O}_5)$ .

**[0041]** In Figures 1 to 4 the localizing of information containing particles on a SEM, using backscattered electron detection, is shown. The inorganic particles in these cases had the composition  $(\text{Y}_{2-u-v-w-x}\text{Nd}_u\text{Gd}_v\text{Er}_w\text{Yb}_x)\text{O}_2\text{S}$ .

**[0042]** Figure 6 shows a table of SEM/EDX analyses, obtained on inorganic particles according to the invention. The first column shows SEM/EDX results, as obtained on the neat particle of Figure 4, using the instrument's internal standardisation and algorithms against the elemental ratio of the standard particle which will only be available to the owner of said standard. Columns 2,3 and 4 show SEM/EDX owner of said standard. Columns 2,3 and 4 show SEM/EDX results for each an individual crystal of the marker, present at concentrations of 1 % and 0.1 %, respectively, in two different intaglio inks. These analyses were performed on customary printing of these inks.

**[0043]** The enhanced coding capacity of this type of marking according to the present invention, as well as its resistance to perturbing elements and to reverse-engineering attempts, will be illustrated with the help of the following example:

Example:	
Encoding particles P1	$(\text{Y}_{1.6}\text{Nd}_{0.2}\text{Gd}_{0.2})\text{O}_2\text{S}$
Encoding particles P2	$(\text{Y}_{1.0}\text{Gd}_{0.6}\text{Yb}_{0.4})\text{O}_2\text{S}$
Encoding particles P3	$(\text{Y}_{1.3}\text{Nd}_{0.1}\text{Gd}_{0.4}\text{Yb}_{0.2})\text{O}_2\text{S}$
Camouflaging material C1	$\text{La}_2\text{O}_3$
Camouflaging material C2	$\text{Gd}_2\text{O}_3$

An encoding realised with a 1:1 mixture of P1 and P2 can be distinguished, according to the present invention, from an encoding realised with P3. US 5,670,239 would not distinguish between both cases. This illustrates the higher coding capacity of the marking means according to the present invention.

[0044] An encoding realised with an 1:1 mixture of P1 and the camouflaging material C1 is easily decoded, according to the present invention, as having the element ratio ( $Y_{1.6}Nd_{0.2}Gd_{0.2}$ ); it is indeed sufficient to localize one crystal of the ( $Y_{1.6}Nd_{0.2}Gd_{0.2}$ )O<sub>2</sub>S particle and to analyse it. Since US 5,670,239 would additionally consider the La<sub>2</sub>O<sub>3</sub>, it would conclude to an overall element ratio of ( $La_{1.0}Y_{0.8}Nd_{0.1}Gd_{0.1}$ ) in this case. This would also be the compositional ratio obtained with classical elementary analysis, X-ray fluorescence, Laser-Ablation-ICP-MS, etc., which illustrates the higher resistance against reverse-engineering of a marking means according to the present invention.

[0045] The same is true for an encoding realised with a mixture of P1 and the camouflaging material C2. SEM/EDX is still in a position to properly read the coding, whereas other analytical methods will result in a totally wrong gadolinium content. This illustrates the robustness of the coding according to the present invention against perturbing elements, which may be present for another reason in or on the coded article. On the other side camouflaging material can purposely be added to mislead any potential counterfeiter.

## Claims

1. Use of at least one inorganic particle comprising at least one predefined ratio of at least two chemical elements as a marking means, wherein said predefined ratio represents a code or part of a code and wherein said particle is selected from the group of non-stoichiometric crystals.
2. Use of at least one particle according to claim 1, wherein said inorganic particle is selected from the group consisting of non-stoichiometric crystals having garnet-, spinel-, perovskite- or zircon-structures.
3. Use of at least one particle according to claim 1, wherein said inorganic particle is selected from the group of non-stoichiometric oxysulfides of rare-earth elements and/or yttrium.
4. Use of at least one particle according to one of the claims 1 to 3, wherein the volume of said particle is comprised within the range of between 0.01  $\mu\text{m}^3$  to 10,000  $\mu\text{m}^3$ .
5. Use of at least one particle according to one of the claims 1 to 4, wherein said particle is held in place in a carrier medium for analysis of said predefined ratio of said chemical elements.
6. Use of at least one particle according to one of the claims 1 to 5, wherein the particle is capable of being localized by scanning electron microscope.
7. Use of at least one particle according to one of the claims 1 to 5, wherein said inorganic particle is capable of being localized on an electron microscope using backscattering electron detection.
8. Use of at least one particle according to one of the claims 1 to 7, wherein said ratio of chemical elements is capable of being analyzed by energy- or wavelength-dispersive X-ray analysis on a scanning electron microscope.
9. Use of at least one particle according to one of the claims 1 to 8, wherein said particle has additionally one or more of the following properties: luminescence, magnetism, IR-absorption, radio-frequency and/or microwave resonance.
10. Use of at least one particle according to any of the preceding claims for marking security documents.
11. Coating composition or printing ink or materials such as paper, security foil, plastic card or fiber, said material comprising particles according to anyone of the claims 1 to 9, wherein the predefined ratio of at least two chemical elements in said particle is used as the marking characteristic and wherein said particles being comprised in amounts ranging from 0.0001% to 10% by weight of the total weight of the overall coating composition, ink or material to which it is added.
12. Method for identifying an article, comprising the steps of:
  - (a) Providing an article comprising at least one inorganic particle according to any one of claims 1 to 9 as a marking, wherein the predefined ratio of at least two chemical elements in said particle represents a code or part of a code;
  - (b) localizing the position of said particle within said article by an analytical means;

(c) analyzing said ratio or ratios of the chemical elements comprised in said particle localized in step (b).

13. Method according to claim 12, further comprising the step of incorporating into said article one or more camouflaging compounds comprising at least one of the chemical elements forming part of said predefined ratio in said particle.
14. Method according to one of the claims 12 or 13 wherein the analyzing means is a scanning electron microscope.
15. Method according to one of the claims 12 to 14 wherein said analysis is performed by energy- or wavelength-dispersive X-ray analysis on a scanning electron microscope.
16. Method according to one of the claims 12 to 15 wherein said particle is localized using backscattered electron detection.
17. Article made from paper or plastic, comprising at least one inorganic particle according to any one of claims 1 to 9 as a marking, wherein the predefined ratio of at least two chemical elements in said particle represents a code or part of a code.
18. Article according to claim 17, wherein said article is a security document such as a banknote, a valued papers, an identity document, a plastic card, or a security foil.

#### Patentansprüche

1. Verwendung wenigstens eines anorganischen Partikels, umfassend wenigstens ein vorbestimmtes Verhältnis von wenigstens zwei chemischen Elementen als ein Markierungsmittel, wobei das vorbestimmte Verhältnis einen Code oder den Teil eines Codes repräsentiert und wobei das Partikel ausgewählt ist aus der Gruppe von nicht-stöchiometrischen Kristallen.
2. Verwendung mindestens eines Partikels gemäß Anspruch 1, wobei das anorganische Partikel ausgewählt ist aus der Gruppe, bestehend aus nicht-stöchiometrischen Kristallen, welche Granat-, Spinell-, Perowskit- oder Zirkonstrukturen aufweisen.
3. Verwendung mindestens eines Partikels gemäß Anspruch 1, wobei das anorganische Partikel ausgewählt ist aus der Gruppe von nicht-stöchiometrischen Oxy sulfiden von Seltenerdelementen und / oder Yttrium.
4. Verwendung mindestens eines Partikels gemäß einem der Ansprüche 1 bis 3, wobei das Volumen des Partikels im Bereich von  $0,01 \mu\text{m}^3$  bis  $10000 \mu\text{m}^3$  liegt.
5. Verwendung mindestens eines Partikels gemäß einem der Ansprüche 1 bis 4, wobei das Partikel in einem Carrier-Medium aufgenommen ist zur Analyse des vorbestimmten Verhältnisses der chemischen Elemente.
6. Verwendung mindestens eines Partikels gemäß einem der Ansprüche 1 bis 5, wobei das Partikel durch ein Rasterelektronenmikroskop lokalisiert werden kann.
7. Verwendung mindestens eines Partikels gemäß einem der Ansprüche 1 bis 5, wobei das anorganische Partikel durch ein Elektronenmikroskop unter Verwendung von Rückstreuelektronendetektion lokalisiert werden kann.
8. Verwendung mindestens eines Partikels gemäß einem der Ansprüche 1 bis 7, wobei das Verhältnis der chemischen Elemente durch energie- oder wellenlängen-dispergierende Röntgenanalyse in einem Rasterelektronenmikroskop analysiert werden kann.
9. Verwendung mindestens eines Partikels gemäß einem der Ansprüche 1 bis 8, wobei das Partikel zusätzlich eine oder mehrere der folgenden Eigenschaften aufweist: Lumineszenz, Magnetismus, IR-Absorption, Radiofrequenz und / oder Mikrowellenresonanz.
10. Verwendung mindestens eines Partikels gemäß einem der vorhergehenden Ansprüche zur Markierung von Sicherheitsdokumenten.

11. Beschichtungszusammensetzung oder Druckfarbe oder Materialien wie Papier, Sicherheitsfolie, Plastikkarte oder Faser, wobei das Material Partikel gemäß einem der Ansprüche 1 bis 9 umfasst, wobei das vorbestimmte Verhältnis von mindestens zwei chemischen Elementen in dem Partikel als ein Markierungscharakteristikum verwendet wird und wobei die Partikel in Mengen umfasst sind, die im Bereich von 0,0001 Gew.-% bis 10 Gew.-% des Gesamtgewichts der Gesamt-Beschichtungszusammensetzung, der Druckfarbe oder des Materials, zu dem sie zugegeben sind, liegen.  
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12. Verfahren zur Identifizierung eines Artikels, umfassend die Schritte:  
10
  - a) Bereitstellen eines Artikels, umfassend mindestens ein anorganisches Partikel gemäß einem der Ansprüche 1 bis 9 als eine Markierung, wobei das vorbestimmte Verhältnis von wenigstens zwei chemischen Elementen in dem besagten Partikel einen Code oder einen Teil eines Codes repräsentiert;
  - b) Lokalisieren der Position des Partikels innerhalb des Artikels durch ein Mittel zur Analytik;
  - c) Analysieren des Verhältnisses oder der Verhältnisse der chemischen Elemente, die in dem Partikel enthalten sind, welcher in Schritt b) lokalisiert wurde.15
13. Verfahren nach Anspruch 12, ferner umfassend den Schritt des Inkorporierens in den Artikel von einer oder mehreren Tarnverbindungen, umfassend mindestens eines der chemischen Elemente, welches einen Teil des vorbestimmten Verhältnisses in dem Partikel bildet.  
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14. Verfahren nach einem der Ansprüche 12 oder 13, wobei das Mittel zur Analytik ein Rasterelektronenmikroskop ist.
15. Verfahren nach einem der Ansprüche 12 bis 14, wobei die Analyse durch energie- oder wellenlängen-dispergierende Röntgenanalyse in einem Rasterelektronenmikroskop durchgeführt wird.  
25
16. Verfahren nach einem der Ansprüche 12 bis 15, wobei das Partikel unter Verwendung von Rückstreuelektronendetektion lokalisiert wird.
17. Artikel, hergestellt aus Papier oder Plastik, umfassend mindestens einen anorganischen Partikel gemäß einem der Ansprüche 1 bis 9 als eine Markierung, wobei das vorbestimmte Verhältnis von wenigstens zwei chemischen Elementen in dem Partikel einen Code oder einen Teil eines Codes repräsentiert.  
30
18. Artikel nach Anspruch 17, wobei der Artikel ein Sicherheitsdokument, wie eine Banknote, Wertpapiere, ein Identifizierungsdokument, eine Plastikkarte oder eine Sicherheitsfolie ist.  
35

#### Revendications

1. Utilisation d'au moins une particule minérale qui comprend au moins un rapport prédéfini entre au moins deux éléments chimiques comme moyen de marquage, ledit rapport prédéfini représentant un code ou une partie de code, et ladite particule étant choisie dans le groupe des cristaux non stoechiométriques.  
40
2. Utilisation d'au moins une particule selon la revendication 1, dans laquelle ladite particule minérale est choisie dans le groupe constitué de cristaux non stoechiométriques qui présentent une structure de grenat, une structure de spinelle, une structure de pérovskite ou une structure de zircon.  
45
3. Utilisation d'au moins une particule selon la revendication 1, dans laquelle ladite particule minérale est choisie dans le groupe constitué d'oxysulfures non stoechiométriques d'éléments de terre rare et/ou d'yttrium.
- 50 4. Utilisation d'au moins une particule selon l'une quelconque des revendications 1 à 3, dans laquelle le volume de ladite particule est compris dans la plage de 0,01  $\mu\text{m}^3$  à 10000  $\mu\text{m}^3$ .
- 55 5. Utilisation d'au moins une particule selon l'une quelconque des revendications 1 à 4, dans laquelle ladite particule est immobilisée dans un substrat pour analyser ledit rapport prédéfini entre lesdits éléments chimiques.
6. Utilisation d'au moins une particule selon l'une quelconque des revendications 1 à 5, dans laquelle la particule peut être localisée au moyen d'un microscope électronique à balayage.



7. Utilisation d'au moins une particule selon l'une quelconque des revendications 1 à 5, dans laquelle ladite particule minérale peut être localisée par un microscope électronique au moyen d'une détection électronique par rétrodiffusion.
- 5 8. Utilisation d'au moins une particule selon l'une quelconque des revendications 1 à 7, dans laquelle ledit rapport entre les éléments chimiques peut être analysé au moyen d'une analyse aux rayons X à dispersion d'énergie ou de longueur d'onde effectuée sur un microscope électronique à balayage.
- 10 9. Utilisation d'au moins une particule selon l'une quelconque des revendications 1 à 8, dans laquelle ladite particule présente en outre l'une ou plusieurs des propriétés suivantes : la luminescence, le magnétisme, l'absorption infrarouge, la résonance aux fréquences radio et/ou aux micro-ondes.
- 15 10. Utilisation d'au moins une particule selon l'une quelconque des revendications précédentes pour marquer des documents de sécurité.
- 20 11. Composition de revêtement ou encre ou matériaux d'imprimerie, par exemple du papier, une feuille de sécurité, une carte ou une fibre en matière plastique, ledit matériau comprenant des particules selon l'une quelconque des revendications 1 à 9, le rapport prédéfini entre au moins deux éléments chimiques présents dans ladite particule servant de caractéristique de marquage, et lesdites particules étant comprises en quantité de 0,0001 % à 10 % en poids du poids total de toute la composition de revêtement, de toute l'encre ou de tout le matériau auquel elles sont ajoutées.
- 25 12. Procédé pour identifier un objet, qui comprend les étapes qui consistent à :
  - (a) mettre à disposition d'un objet qui comprend comme marqueur au moins une particule minérale selon l'une quelconque des revendications 1 à 9, le rapport prédéfini entre au moins deux éléments chimiques présents dans ladite particule représentant un code ou une partie de code,
  - (b) localiser la position de ladite particule dans ledit objet à l'aide d'un moyen analytique,
  - 30 (c) analyser ledit ou lesdits rapports entre les éléments chimiques présents dans ladite particule localisée à l'étape (b).
- 35 13. Procédé selon la revendication 12, qui comprend en outre l'étape d'incorporation dans ledit objet d'un ou de plusieurs composés de camouflage qui comprennent au moins l'un des éléments chimiques qui font partie dudit rapport prédéfini dans ladite particule.
- 40 14. Procédé selon la revendication 12 ou la revendication 13, dans lequel le moyen d'analyse est un microscope électronique à balayage.
- 45 15. Procédé selon l'une quelconque des revendications 12 à 14, dans lequel ladite analyse est réalisée au moyen d'une analyse par rayons X à dispersion d'énergie ou de longueur d'onde sur un microscope électronique à balayage.
- 50 16. Procédé selon l'une quelconque des revendications 12 à 15, dans lequel ladite particule est localisée au moyen d'une détection électronique par rétrodiffusion.
- 55 17. Objet formé de papier ou de plastique, qui comprend comme marqueur au moins une particule minérale selon l'une quelconque des revendications 1 à 9, dans lequel le rapport prédéfini entre au moins deux éléments chimiques présents dans ladite particule représente un code ou une partie de code.
18. Objet selon la revendication 17, dans lequel ledit objet est un document de sécurité, par exemple un billet de banque, un document de valeur, un document d'identité, une carte en matière plastique ou une feuille de sécurité.

Fig. 1

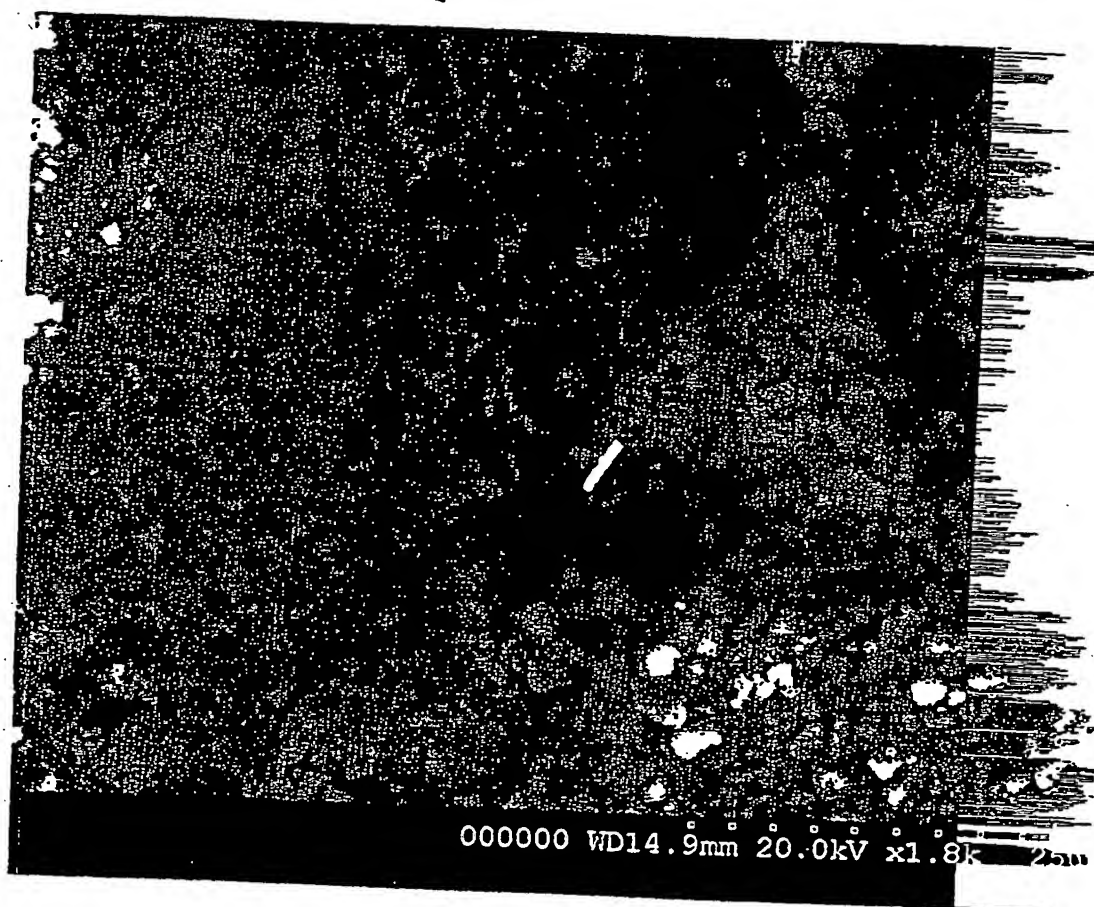


Fig. 2

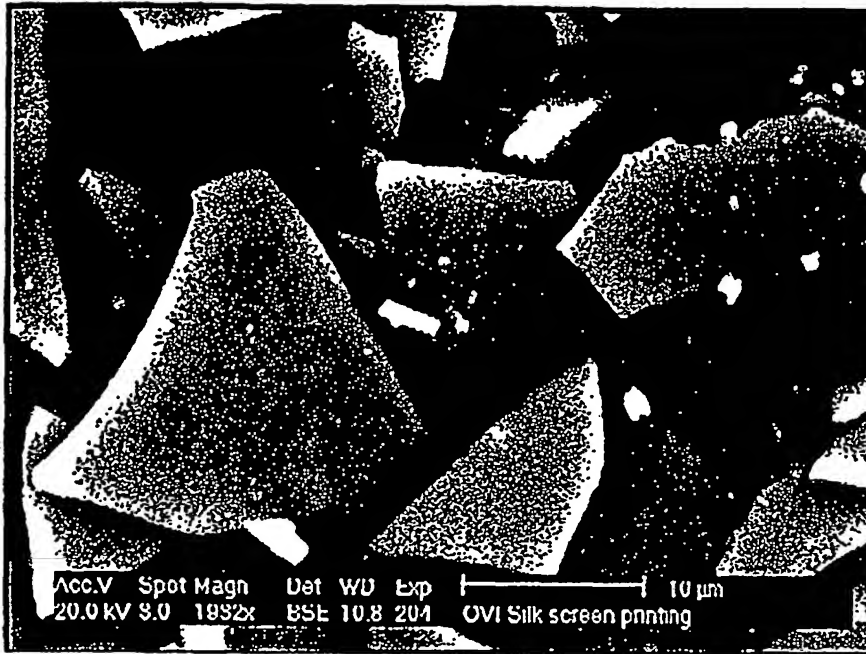


Fig. 3

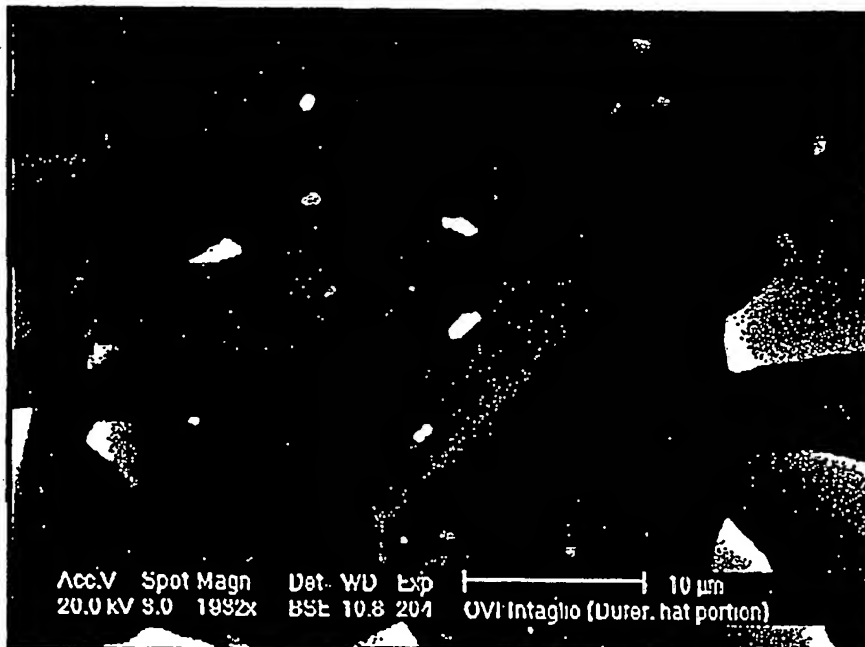


Fig. 4



Fig. 5

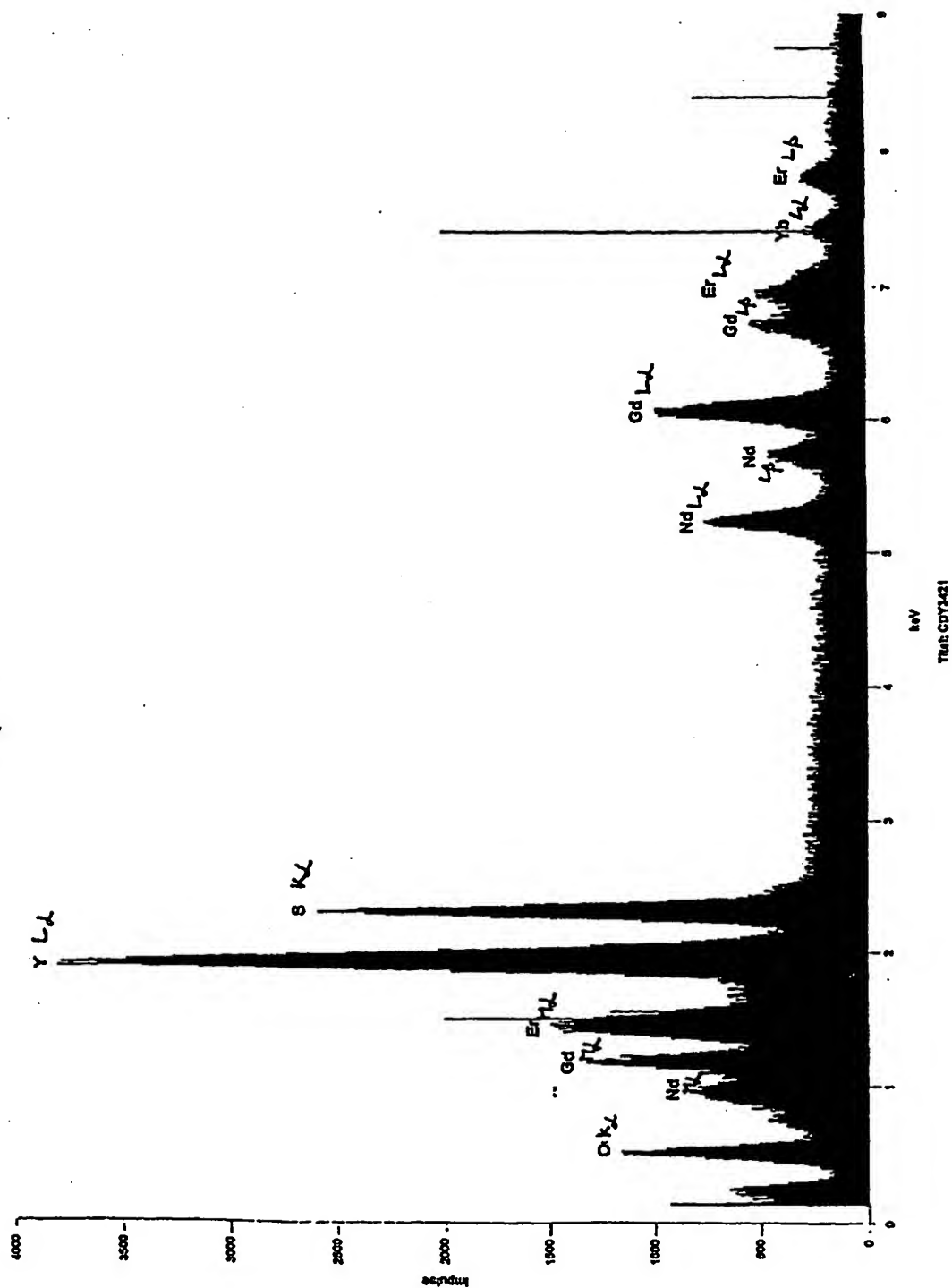


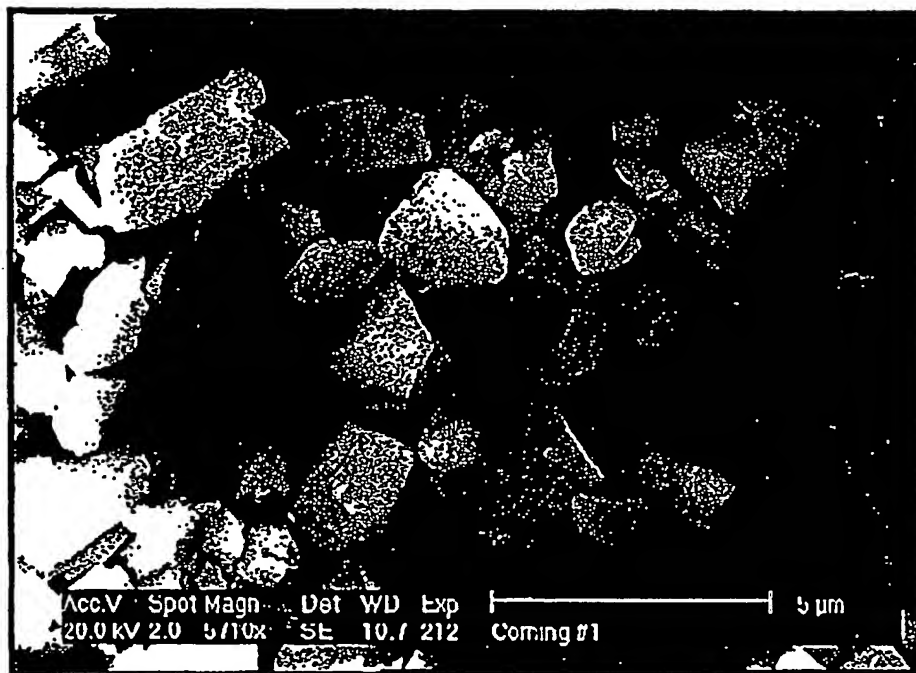
FIG. 6

Table of Analyses

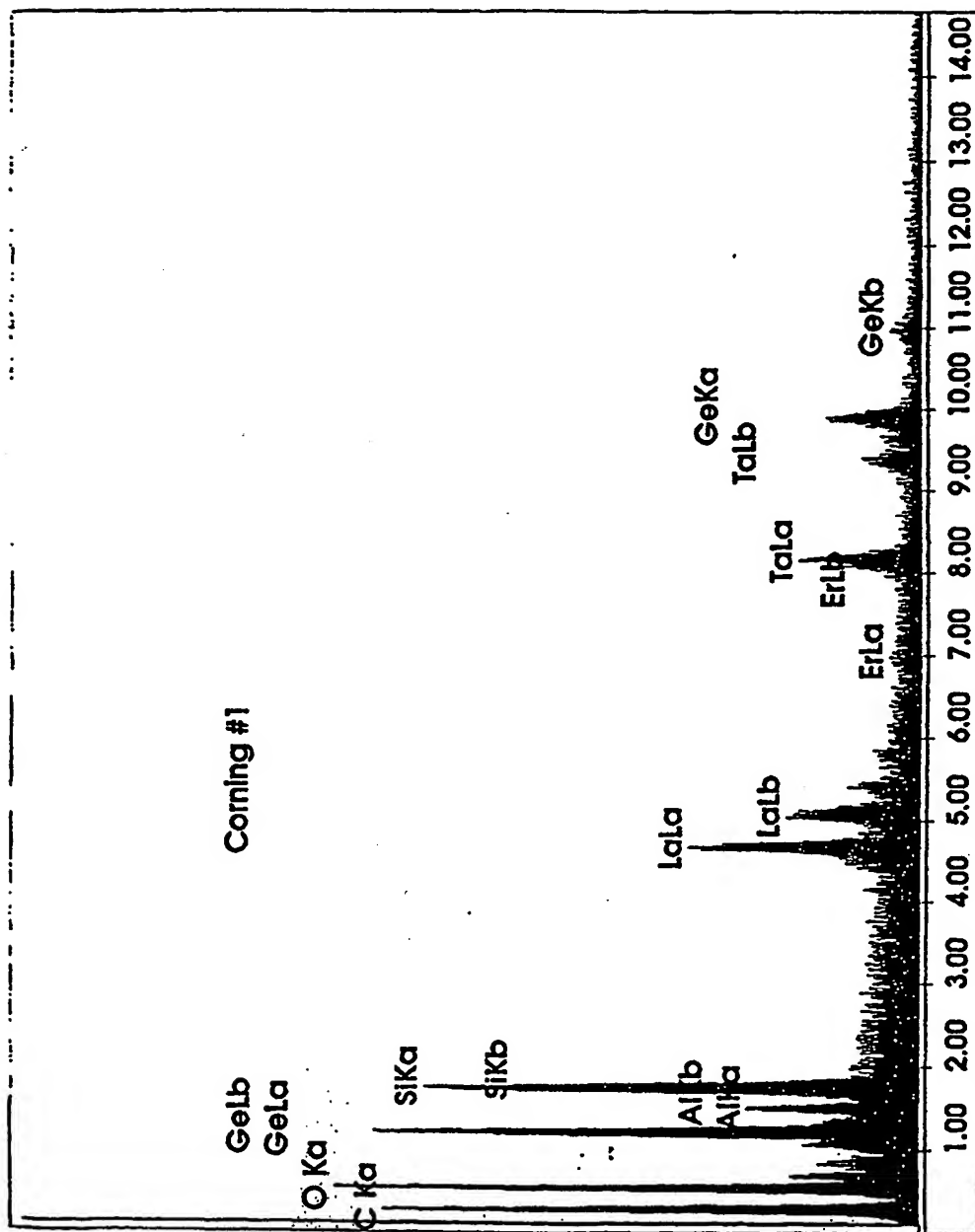
	SEM/EDX analysis of marking composition (bulk material)	SEM/EDX analysis of 1% of marking composition in printed intaglio ink I	SEM/EDX analysis of 1% of marking composition in printed intaglio ink II	SEM/EDX analysis of 1% of marking composition in printed intaglio ink II
$Y_2O_2S$	47.43	43.35	44.03	47.22
$Nd_2O_2S$	13.17	14.42	15.72	13.07
$Gd_2O_2S$	22.72	27.14	25.11	24.59
$Er_2O_2S$	9.29	9.17	8.34	10.66
$Yb_2O_2S$	7.40	5.91	6.81	4.46
	100.01	99.99	100.01	100.00

The values are given in percentages of equivalent oxysulphides  $M_2O_2S$

Fig. 7



**Fig. 8**





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